Pergamon

Tetrahedron Letters, Vol. 38, No. 40, pp. 7057-7058, 1997

0040-4039/97 $17.00 + 0.00

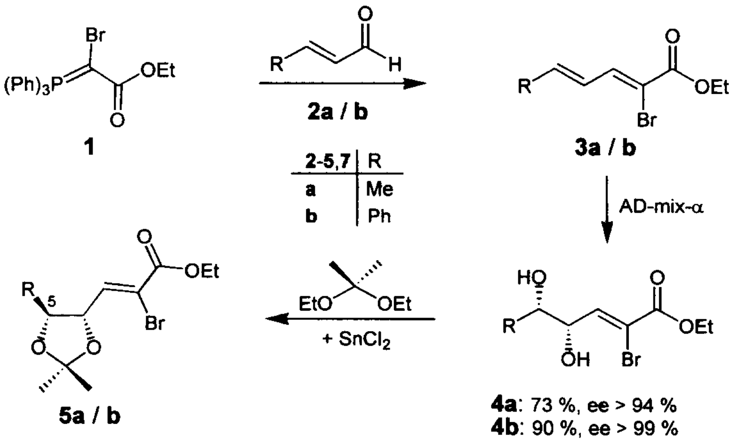
PII: S0040-4039(97)01648-1

Synthesis and Reactions of Chiral 5-Substituted (*Z*)-Ethyl 2-Bromo-3-(1,3-dioxolan-4-yl)-2-propenoates

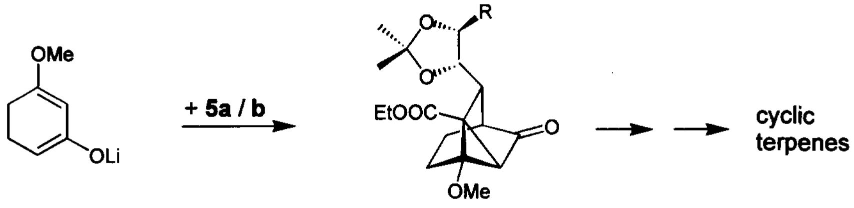
Norbert A. Braun, Ulrike Bürkle, Iris Klein, Dietrich Spitzner*
Institut für Chemie, Abt. Organische Chemie, Universität Hohenheim, Garbenstraße 30,
D-70599 Stuttgart, Germany

Abstract: Wittig olefination of the aldehydes **2a/b** gave the 2-bromo-dienes **3a/b**. Regioselective catalytic Sharpless asymmetric dihydroxylation (AD) led to the diols **4a/b** with high enantiomeric excess (ee > 94 %). Cascade reactions of **5a/b** with dienolate **6** yielded **7a/b** with excellent diastereomeric excess (de > 95 %). © 1997 Elsevier Science Ltd.

Enantiopure α-halo-α,β-unsaturated esters of type **5** (R = H) are useful precursors for the synthesis of aziridine derivatives[1] and various types of terpenoid natural products[2]. There are basically two convenient methods for the synthesis of 5-unsubstituted α-halo esters **5** (R = H): the Peterson olefination and the Wittig- or Horner-Emmons olefination. The chiral moiety is derived from D-mannitol.[3] We report here about the synthesis of chiral 5-substituted α-halo-α,β-unsaturated esters **5a/b** (R = Me, Ph) from easily accessible prochiral dienes **3a/b** by the catalytic asymmetric Sharpless dihydroxylation (AD).[4]



The 2-bromo-dienes **3a/b** were obtained by Wittig olefination of bromophosphorane **1** with aldehydes **2**.[5] Oxidation of the prochiral **3a/b** with AD-mix-α led only to the (*Z*)-diols **4a/b** in excellent enantiomeric excess. No attack of the $\Delta^{2,3}$-bond was observed.[6] The configuration of the $\Delta^{2,3}$-bond was determined by measuring the ^{3}J(C,H) coupling.[7] We applied the "mnemonic device" to estimate the face selectivity in this dihydroxylation.[6b] Protection of the *cis*-diol of the compounds **4a/b** with diethoxypropane/$SnCl_2$ gave the acetales **5a/b**, which were used as Michael acceptors for anionically induced cascade reactions with the lithium dienolate **6**. The resulting tricyclo[3.2.1.0^{2,7}]octanes **7a/b** were formed with excellent diastereomeric excess.[8] The absolute stereochemistry of **7b** was determined by X-ray structure analysis[9] while the absolute configuration of **7a** was deduced from the CD spectrum which is similar to the spectra of both **7b** and **7** (R = H).[2]



6

7a: 48 %, de > 95 %
7b: 29 %, de > 95 %

ACKNOWLEDGEMENTS: We thank the *Deutsche Forschungsgemeinschaft*, Bonn, the *Fonds der Chemischen Industrie e.V.*, Frankfurt (Main), and the *DAAD*, Bonn, for financial support within the "Vigoni-Programm" and Chemetall GmbH, Frankfurt (Main), for generous gifts of chemicals. N. A. B. thanks the *Landesgraduiertenförderung*, Baden-Württemberg, for a scholarship.

REFERENCES AND NOTES

1. a) Ambrosi, H.-D.; Duczek, W.; Ramm, M.; Gründemann, E.; Schulz, B.; Jähnisch, K. *Liebigs Ann. Chem.* **1994**, 1013-1018, b) Ambrosi, H.-D.; Duczek, W.; Ramm, M.; Jähnisch, K. *Tetrahedron Lett.*, **1994**, *35*, 7613-7616.
2. a) Braun, N. A.; Klein, I.; Spitzner, D; Vogler, B.; Braun, S.; Borrmann, H.; Simon, A. *Liebigs Ann. Chem.* **1995**, 2165-2169, b) Braun, N.A.; Spitzner, D. *Tetrahedron Lett.*, **1996**, *37*, 9187-9188.
3. Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447-488.
4. Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483-2547. We thank Professor K. B. Sharpless for helpful discussions.
5. Märkl, G. *Chem. Ber.* **1961**, *94*, 2996-3004.
6. a) Becker, H.; Soler, M. A.; Sharpless, K. B. *Tetrahedron* **1995**, *51*, 1345-1376, b) Kolb, H. C.; Andersson, P. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1994**, *116*, 1278-1291, c) ee were determined on a CHIRALCEL OD column, Daicel. We thank Professor B. Danieli, Universita degli Studi di Milano, and his group for assistance.
7. **4b**: $^{3}J(^{13}C,^{1}H) = 4.8$ Hz .We thank Dr. S. Braun, TH Darmstadt, for this experiment.
8. All new compounds (**3b**, **4**, **5** and **7**) have been fully characterized. **4b**: ^{13}C NMR (300 MHz, $CDCl_3$):δ = 14.03 (q), 62.85 (t), 75.56 (d), 75.60 (d), 117.85 (s, C–2), 126.46 (d), 128.26 (d), 128.48 (d) 139.47 (s), 143.16 (d, C–3), 161.90 (s, C–1); $[\alpha]_D^{24} = -16.2$ ($c = 0.61$, $CHCl_3$).
9. Peters, K.; Peters, E.-M.; Braun, N. A.; Klein, I.; Spitzner, D. *Z. Kristallogr.*, in press.

(*Received in Germany* 30 *June* 1997; *accepted* 8 *August* 1997)